Accumulation of Polychlorinated Biphenyls in Ecosystems

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Chlorinated biphenyl compounds have become ubiquitous components of the global environment. They were first detected in species of Swedish wildlife (1, 2, 3) and were subsequently found in seals from the North Atlantic (4), in a bird of prey in Great Britain (5), in fish and birds from the Netherlands (6), and in both terrestrial and marine species of wildlife in western North America (7). In the Arctic they are present in the polar bears (*Thalarctos maritimus*) of Hudson Bay (8) and in fresh-water fish of tundra lakes that receive no pollutants save those that are present in the fallout from the atmosphere (9). In the Southern Hemisphere, they were found in all bird species analyzed that inhabit waters north of the Antarctic Convergence but could not be detected in a number of samples of wildlife resident in Antarctica south of the Convergence (10). In this paper some of the available residue data are summarized within the framework of a preliminary formulation of a mass balance equation for the global distribution of polychlorinated biphenyls.

Commercial manufacture of PCBs was begun in the United States in 1929 (11), and environmental input may be assumed to have begun at that time. Current levels of PCBs in major sinks, such as the oceans, are evidently a function of many parameters, including the proportion of the total amount of PCBs produced over the past forty years that has so far entered the environment, pathways of dissemination, rates of degradation to other compounds, partition coefficients between water and lipid fractions of organisms and the rates of permanent deposition in the sediments. The determination of accumulation rates in major sinks and the prediction of levels to be expected in the future, given estimates of global production and of environmental input, constitute a challenging problem in environmental science.

A mass balance equation that would predict future levels of PCBs in the sea might profitably be modeled on the approach recently used by Weiss et al. (12) in considering the amount of mercury introduced to the sea as a result of the activities of man. Like PCBs, mercury in its various chemical forms is not essential to organisms but may be accumulated by them. Both groups of compounds move through the environment by water and air transport and are mobilized from pools that exist in a variety of industrial products, in addition to the pool of mercury in the earth's crust. The transfer of mercury from the continents to the oceans in river runoff was estimated to be at most 2.8×10^{9} grams per year, considerably less than the estimated rate of exchange between the continents and the atmosphere, between 2.5×10^{10} and 1.5×10^{11} grams per year. The latter figures were obtained from measurements of mercury in rainwater of the 1930's and in uncontaminated glacial ice. The amount of mercury produced by man per year is currently on the order of 10^{10} grams, of which one third was estimated to enter the atmosphere. Other sources of atmospheric mercury include the burning of fossil fuels, cement production and mining operations, but the integrated input resulting from man's activities in industry and agriculture was less than that released into the atmosphere by natural processes. The doubling of the mercury content in dated layers of snow from a Greenland

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ice sheet over the past several decades was attributed to an increased disturbance of sedimentary rocks as a result of human disturbance (12).

Such an approach yielded the prediction that the current mercury content of marine organisms is at most no more than double that present in pre-technological times (12).

The only synthetic pollutant for which a comparable mass balance approach has been formulated is the insecticide DDT, together with its derivatives (13). Over the past fifteen years about 6×10^{10} grams per year of DDT have been manufactured in the United States, of which a considerable fraction is exported. The total global production per year was estimated to be in the order of 10^{11} grams (13), of which all may be assumed to be released into the environment. Analyses of DDT concentrations in river waters indicated that only a small fraction of the DDT applied to the land would reach the sea by river transport. The few data available for DDT concentrations in precipitation indicated, however, that as much as one quarter of the global production and use could be transported to the sea through the atmosphere (13, 14). Yet the total amount of DDT compounds estimated to be in pelagic marine organisms was only 10^8 grams. Evidently additional measurements of DDT in marine precipitation and in the water and organisms of the mixed layer are required before the mass balance approach can be used to predict future levels of DDT compounds in the oceans.

The ubiquity of the PCB compounds and their relatively high concentrations in marine organisms of certain areas require that an approach now be made toward the formulation of a mass balance equation in the global environment, as a necessary step in the implementation of a program that would prevent the buildup of unacceptable levels.

At the request of a number of environmental scientists concerned about the possibility that PCB levels would continue to increase in the sea, the Monsanto Company has recently released the total production figures for their Aroclor PCB products from 1960 through 1970, with estimated figures for production in 1971. Total U.S. production of the combined total of all PCB products rose steadily between 1960 and 1970, from approximately 2×10^{10} grams in 1960 to approximately 4×10^{10} grams in 1970. Estimated production figures for 1971, however, show a sharp drop from those of 1970 and are equivalent to 1960 levels. Approximately half of this amount is used in "closed system" applications as electrical insulating liquids. The domestic sales for all other uses, including heat transfer systems, hydraulics and lubricants, plasticizers, etc., rose from approximately 5×10^9 grams in 1960 to about 1.5×10^{10} grams in 1970, but estimated sales in 1971 were far below the 1960 figures. A considerable fraction of PCBs used in the "open system" applications can be expected eventually to enter the environment. U.S. export sales showed approximately no change between 1960 and 1965 and were in the order of 2×10^9 grams per year but have since risen to about 5×10^9 grams (15). Of the other industrialized countries that produce chlorinated biphenyl compounds, notably France, Germany, Italy, Japan, and the Soviet Union, production figures are apparently readily available only from Japan where PCBs are manufactured by two companies, the Kanegafuchi Chemical Industry and the Mitsubishi-Monsanto Chemical Company, with combined production figures on the order of 10^{10} grams per year, somewhat less than the estimated 1971 total U.S. production of 2.0×10^{10} grams. In 1970, 60% of the PCBs produced in Japan were used for insulating fluids of capacitors and transformers, 15–20% for the solvent in carbonless reproducing paper, 10% for heat-transfer media, and 5–10% as plasticizers and for export (16).

The figures made public by Monsanto were for total PCB production only. The chlorine composition of the PCBs detected in marine systems may vary widely between that in waste water outfalls and in the tissues of fish-eating birds (17, 18). It is therefore essential to have production figures for each class of PCBs in order to understand PCB movements into and through marine ecosystems. These have been presented in the previous paper.

Combined U.S. and Japanese figures for 1970 were, therefore, on the order of 5×10^{10} grams. A reasonable estimate for global production figures, including the PCBs manufactured in the Soviet Union and Western Europe, is therefore on the order of 10^{11} grams per year, equivalent to those of DDT.

Few data are yet available that permit calcu-

lations of the amounts of PCBs transferred to the sea. Holden (19) found that about one ton of PCBs per year was entering the estuary of the Clyde as a component of crude sewage sludge from the Glasgow district. Approximately a ton of PCBs was also entering the estuary of the Thames as a component of sewage sludge from London. Comparable amounts of PCBs were found to be entering the Pacific Ocean from each of several waste water outfalls in California (17). The evidence for atmospheric dissemination of PCBs derives from their virtually universal distribution in the global environment, including resident Arctic species (9) and from the detection of PCB peaks in all samples of rain water obtained over a year at seven widely distributed sites in Great Britain (14). These PCBs were not quantitated. Permanent snow fields provide a historical record of PCB deposition with time. The possibility therefore exists for measuring the total amount of PCBs transferred from the atmosphere to snow fields receiving fallout from the major wind systems.

Measurements of PCB concentrations in the mixed layer of the ocean or in deeper waters have not yet been made. Concentrations in collections of zooplankton from the Atlantic, however, are surprisingly high. Samples from eleven stations over the Continental Shelf and Slope areas east of the northeastern United States contained a median concentration of 57 ppm PCBs, with a range from 2 to 260 ppm, in the extractable lipids, defined as all materials extracted in a Soxhlet apparatus with 2:1 hexane:acetone. Median dry and wet weight concentrations were on the order of 2 and 0.2 ppm respectively. Comparable values were obtained in samples from two stations near Bermuda and from two stations in the South Atlantic in the wind path from the industrialized areas of Brazil. Concentrations of PCBs in two samples from the eastern South Atlantic were lower by an order of magnitude (20). Because of wide differences in the total mass of zooplankton per unit volume of water, the values obtained in analyzing zooplankton samples are an imperfect indication of the local burden of PCBs. Moreover, partition coefficients between PCB concentrations in sea water and in zooplankton might be expected to depend on the nature of the lipids and other nonpolar substances in which PCBs accumulate.

Quantitation procedures for PCBs have not yet been standardized. In many waste water and biological samples, however, the profile of PCB peaks closely matches one of the commercial preparations, and accurate quantitation can then be made using the height of any one of the prominent peaks. The Atlantic zooplankton and fish samples from Long Island Sound (21) had a PCB composition that closely matched that of Aroclor 1254. Other environmental samples, particularly birds (10, 18), frequently have a PCB composition that is intermediate between 54 and 60 per cent chlorine. An arbitrary decision must therefore be made which may affect the values obtained by a factor as much as 2 or more. Most of the PCB values reported in papers from our laboratory have been obtained by comparing the total area of all PCB peaks emerging after p,p'-DDE to the total areas of the same peaks in chromatograms of the Aroclor 1254 standard. These values may be somewhat too high. Samples may contain a lower proportion of the PCB compounds with fewer chlorine atoms than does the 1254 standard. Also, the biphenyl molecules with more chlorine atoms have a greater ability to capture electrons and give, in general, proportionately greater responses in the electron capture detector per molecule of biphenyl. Thus, two eggs of the Common Tern, *Sterna hirundo*, from the colony on Great Gull Island, Long Island Sound, were quantitated for PCBs using two different methods. The areas of PCB peaks emerging after DDE were first compared with the 1254 standard and concentrations of 308 and 214 ppm in the egg lipids were calculated, respectively. When areas were compared with the total areas of the same peaks in chromatograms of the Aroclor 1260 standard, the PCB values obtained were lower by a factor of 2 and were, respectively, 145 and 98 ppm. The column used in this instance was 5% QF-1 on Chromosorb W, 80–100 mesh, acid washed, HMCS treated. Under the conditions employed, the integrated areas of all peaks of chromatograms of equal amounts of Aroclor 1242, 1254, and 1260, respectively, increased in the ratio 1.00:1.68:2.46 (22).

The different quantitation procedures used by various laboratories may be expected to yield, therefore, somewhat different estimates of PCB concentrations. It is reasonable to assume, how-

Table 1. PCB in Marine Fish and in Fish from an Arctic Tundra Lake.

Locality, reference	Species	ppm, fresh weight	ppm, extracted lipid or fat
Tokyo Bay	Sea bass *Lateolabrax japonica*	1.7–3.4	120
Nova Scotia Banks (23)	Atlantic salmon *Salmo salar*	0.45	—
	Atlantic herring *Clupea harengus*	0.32–0.54	—
	Atlantic mackerel *Scomber scombrus*	0.35	—
	Cod *Gadus morhua*	0.02	—
Swedish West Coast (2)	Cod *Gadus morhua*	0.02	7.3
	Fish oil	—	0.7
Baltic Sea (2)	Atlantic herring *Clupea harengus*	0.27	6.8
	Cod *Gadus morhua*	0.03	11
	Atlantic salmon *Salmo salar*	0.30	2.9
	Fish oil	—	3.5
North Atlantic (24)	Flying Fish *Cypselurus exsiliens*	0.001–0.007	0.4–0.5
	Dolphin *Coryphaena hippurus*	0.01	10
	Shark (liver) *Carcharhinus longimanus*	0.3	0.6
	Mesopelagic Fish *Chauliodus danae* 800–900 meters	0.01–0.06	1.5–7.3
Long Island Sound (21)	Atlantic round herring *Etrumeus teres*	1.2	30
	Atlantic silverside *Menidia menidia*	3.2	52
	Atlantic mackerel *Scomber scombrus*	1.2	79
California Coastal Waters (25)	Northern anchovy *Engraulis mordax*	1.0	—
	Jack mackerel *Trachurus symmetricus*	0.02	—
	Bluefin tuna *Thunnus thynnus*	0.04	—
Peruvian Coastal Waters (26)	Sardina peruana *Sardinops sagax*	0.01	0.6
	Caballa *Scomber japonicus*	0.02	2.0
	Bonito *Sarda sarda*	0.01	0.5
	Tiburón azul *Prionace glauca*	0.08	11.4
Lake Minto Ungava, Quebec (9)	Lake trout *Salvelinus namaycush*	0.04–0.6	1.1–12.0

(—) = Concentrations in parts per million.

ever, in comparing these results, that differences of an order of magnitude would yield useful information on geographical distribution.

In Table 1 are summarized some of the reported PCB residue data in fish from representative areas of the oceans and, for comparison, PCB values obtained in lake trout, *Salvelinus namaycush*, from a remote Arctic lake. Among these, highest concentrations were in the fish from Tokyo Bay and from Long Island Sound (Table 1). These bodies of water can be expected to receive significant amounts of PCBs from urban sewage outfalls. A comparison of the residues in three species, the Atlantic salmon, *Salmo salar*, the Atlantic herring, *Clupea harengus*, and cod, *Gadus morhua*, from the Nova Scotia banks and from Swedish waters shows that both areas have comparable levels of PCB contamination. That PCBs have penetrated below the mixed surface layer of the North Atlantic is shown by their presence in fish characteristic of deeper waters obtained at depths between 800 and 900 meters. PCBs were also detected in the fish from the coastal waters of Peru. The levels in lake trout from Lake Minto in the Arctic region of Quebec were higher than expected. Lakes in this area are shallow with rocky bottoms, almost no vegetation, and very low amounts of organic matter. It is interesting that levels in the Atlantic herring, a fatty fish, from both the Nova Scotia banks and the Baltic

Table 2. PCB residues in petrels and shearwaters. Mean arithmetic concentrations in parts per million.

Species, reference	Breeding area	Non-breeding area	Tissue (N)	ppm, fresh weight	ppm, liquid lipid
Ashy Petrel (27) *Oceanodroma homochroa*	California coastal waters	California coastal waters	Whole body (9)	21	200 (120–320)
			Egg (6)	37	240 (130–370)
Leach's Petrel (28) *Oceanodroma leuchorhoa*	Baja California, Pacific Coast	Eastern Pacific	Egg (1)	—	350
Black Petrel (7) *Loomelania melania*	Gulf of California	—	Whole body (8)	1.0	—
Least Petrel (7) *Helocyptena microsoma*	Gulf of California	—	Whole body (3)	0.4	—
Fulmar (7) *Fulmarus glacialis*	Alaska	Eastern Pacific	Whole body (3)	2.3	—
Pink-footed Shearwater (7) *Puffinus creatopus*	Chile	Western Mexico, northern Pacific	Whole body (1)	0.4	—
Sooty Shearwater (7) *Puffinus griseus*	New Zealand	Northern Pacific	Whole body (2)	1.1	—
Slender-billed Shearwater *Puffinus tenuirostris* (7)	Australia	Northern Pacific	Whole body (1)	2.1	—
Wilson's Petrel (10) *Oceanites oceanicus*	Hallett Station, Antarctica	Australian seas	Whole body (10)	2.1	11.0
	Palmer Station, Antarctica	North Atlantic	Whole body (9)	33	190
Giant Petrel (10) *Macronectes giganteus*	Palmer Station, Antarctica	Southern oceans	Egg (3)	0.2	3.5
Snow Petrel (10) *Pagodroma nivea*	Hallett Station, Antarctica	Antarctic ice-pack	Whole body (10)	0.08	0.3

were considerably higher, by an order of magnitude, than levels in the cod on a fresh weight basis, although the cod occupies a higher position in the food web. On a fat basis, however, residues in both species in the Baltic were comparable. These data suggest that amounts and kinds of lipids may affect the retention of PCBs, modifying the trophic accumulation predicted by the classical food chain concentration theory. Consistent with this hypothesis are the higher PCB residues measured in extractable lipids of the North Atlantic plankton than in the lipids of fish from the same area.

Table 2 includes a representative selection of PCB residues so far measured in species of petrels and shearwaters. These birds are strictly oceanic, rarely approaching land except to breed on islands or undisturbed coastal areas. They do not dive for their food as do the fish-eating species but rather feed upon plankton and other organic material obtained at the surface of the sea. Within a given marine ecosystem, their burdens of both PCB and DDT residues may be higher than those in fish-eating species such as the Brown Pelican, *Pelecanus occidentalis*, or the Osprey, *Pandion haliaetus* (7). Many species range widely, breeding in one hemisphere and spending the remainder of the year in the other. As expected, lowest levels were found in the Snow Petrel, *Pagodroma nivea*, a species resident in the Antarctic pack-ice region. High residues were found in tissues of the Wilson's Petrel, *Oceanites oceanicus*, from the population that breeds on the Antarctic Peninsula and migrates to the North Atlantic during the southern winter months. Comparable levels were found in the Ashy Petrel, *Oceanodroma homochroa*, a species that remains largely or entirely within the California coastal waters. High PCB concentrations were also found in an egg of a Leach's Petrel, *Oceanodroma leuchorhoa*, obtained on the Islas Coronados, Baja California, Mexico, in the vicinity of San Diego, California (Table 2).

Table 3 summarizes the PCB data obtained from analysis of eggs of the Brown Pelican over a

Table 3. PCB residues in eggs of the Brown Pelican, Pelecanus occidentalis, from North and South America. Mean arithmetic concentrations in parts per million of the egg lipid (30).

Breeding area	Sample size	ppm PCB, lipid
Peru	5	14
Panama	6	4
Venezuela	4	5
Jamaica	4	19
Florida, 4 colonies	87	71
Gulf of California	4	4
San Benitos, Western Baja California	10	39
San Martin, Western Baja California	6	72
Los Coronados	28	266
Anacapa Island, California	65	210

substantial portion of its range in both North and South America. This species feeds only upon marine fish obtained in coastal waters. As expected, levels in the South American populations are substantially lower than those in North America. Concentrations in Florida tend to be about three times lower than those in California. This species does not occur along the coast of the heavily industrialized areas of the northeast United States, but in these areas the Osprey, another fish-eating species, may contain PCB residues five to ten times higher than those in the Florida populations of Brown Pelicans (29). The PCB or associated compounds are a possible cause of embryonic mortality observed in the Osprey populations of these areas (29).

The major difficulty in the design of a monitoring program to determine whether PCB residues are increasing or declining in a given sink is the lack of a statistical design that would establish how many individual specimens should be analyzed in order to determine the parameters of the pollutant distribution at a desired confidence level. Nor has it been established which species of organisms are most suitable for such monitoring programs. The distribution of residues of chlorinated hydrocarbon insecticides and their derivatives within a population is frequently non-Gaussian, although transformation of residue concentrations to their logarithms yields a distribution that is sufficiently Gaussian for the use of established statistical methods (31, 32). Confidence intervals, therefore, can be established for such parameters as the means of logarithms of residue concentrations. The confidence interval, however, cannot be transformed back to the original distribution. There apparently are no satisfactory statistical methods that would determine the confidence intervals about the arithmetic or geometric mean of measured concentrations (32). Moreover, one hundred or more analyses of individual specimens might be necessary to determine the precision of the logarithm of the geometrical mean within a range equivalent to 10% of the value of the geometric mean (31, 32).

The two major research problems that are emerging from the occurrence of PCBs in the environment appear to be first, the determination of the accumulation rates in sinks, so that the concentrations found there might be related to input levels, and second, the determination of the effects of PCBs or their derivatives upon organisms and ecosystems at each contamination level. It might be hoped that a fraction of the considerable sums of money that would be spent at both national and international levels to "monitor" the environment will be diverted to programs designed to answer the significant questions rather than to assemble tables of random numbers, for which there is no pressing need.

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